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Benzimidazolium sulfonate ligand precursors and application in ruthenium-catalyzed aromatic amine alkylation with alcohols

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ABSTRACT

New benzimidazolium sulfonate salts have been prepared and fully characterized. They have been associated *in situ* with $[\text{RuCl}_2(p\text{-cymene})]_2$ to generate efficient catalytic systems operating at 120 °C under neat conditions in the presence of potassium *tert*-butylate for selective *N*-alkylation of primary aromatic amines into secondary amines.

Keywords: Benzimidazolium sulfonates, ruthenium catalysis, *N*-alkylation, hydrogen borrowing

1. Introduction

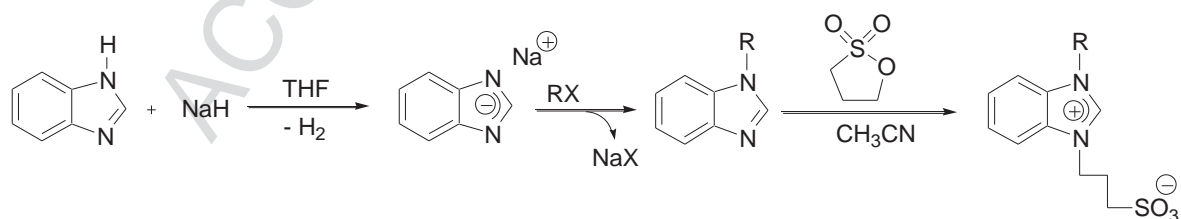
Amines constitute a class of organic compounds with a wide range of applications in chemical industry ranging from ammonia, produced in million ton scale, to fine chemicals with biological properties [1]. In this context, the creation of C-N bonds from primary and secondary amines has been investigated for a long time and more recently using the hydrogen borrowing process starting from alcohol as alkylating agent [2-6]. This methodology offers advantages in terms of atom economy and clean reaction over other methods based on organic or organometallic coupling reactions, as only water is formed as byproduct. *N*-Alkylation of aromatic amines has been mostly carried out with iridium catalyst precursors such as $[\text{Cp}^*\text{IrCl}_2]_2$ in the presence of a carbonate or hydrogenocarbonate as mineral base in refluxing toluene. Intermolecular reaction with alcohols [7] and cyclization with diols [8] have thus been successfully achieved. *N*-alkylation of anilines with iridium catalysts has also been carried out without base additive in water in the presence of $[\text{Cp}^*\text{IrI}_2]_2$ [9] or in neat conditions with dicationic catalysts [10, 11]. Catalytic systems based on ruthenium precursors have proved to be also efficient for aniline *N*-alkylation. Initial results were obtained using $\text{RuCl}_2(\text{PPh}_3)_3$ or $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in the presence of phosphine without additional base but at high temperature (180 °C) with or without a solvent, leading to substituted secondary and tertiary anilines [12], *N*-aryl-substituted cyclic amines [13], and heterocycles [14]. Then, new catalysts were designed in order to introduce milder conditions, especially lower temperature conditions or lower amounts of base. In the iridium series, this was done by implementation of bidentate (C, N), (P, N) and tridentate (P, N, P) ligands, which allowed alkylating aniline below 100 °C at low catalyst loading with $t\text{BuOK}$ or CsOH as base [15, 16]. Phosphine-sulfonate ligands were also introduced on $\text{Cp}^*\text{Ir(III)}$ complexes to achieve the double *N*-alkylation of primary aniline derivatives with pentanediols [17]. *N*-Heterocyclic carbene ligands including chelating ones [18-20] were also used with success. The same strategy was applied to ruthenium catalysts and tridentate nitrogen ligands, (N,N,N) and (P,N,P) pincer ligands were introduced to ruthenium(II) centers but the catalytic *N*-alkylation of aniline still required high temperature [21]. Tridentate (N,N,C) [22] and tetradentate (N,N,N,N) [23] ligands provided efficient catalysts able to operate at 100-110 °C in the presence of a base. More simple ruthenium precursors such as $[\text{Ru}(\text{Cl}_2(\text{cod}))_n]/1,3,5\text{-triazad-7-phosphaadamantane}$ (PTA), [24] $[\text{RuCl}(\text{PPh}_3)(\text{MeCN})_3][\text{BPh}_4]$ [25] or the *in situ* generated system based on $[\text{RuCl}_2(p\text{-cymene})]_2$ and diphosphine ligand were found efficient for the *N*-alkylation of aniline with catalytic amounts of base [26]. However, only scarce examples of ruthenium

complexes bearing a *N*-heterocyclic carbene ligand have been investigated in *N*-alkylation of aromatic amines by alcohols [27]. To our knowledge, $\text{RuX}_2(\text{NHC})(p\text{-cymene})$ ($\text{X} = \text{Cl}, \text{I}$) complexes have revealed good catalytic activity in the reaction of primary aliphatic amines with primary alcohols to form amides but no *N*-alkylation products were formed [28]. Based on the ability of the basic sulfonate group to transfer protons and generate water-soluble species [29], we decided to prepare new *N*-heterocyclic carbene sulfonate ligands constructed on the benzimidazole core, and evaluate their activity in the *N*-alkylation of aniline and 2-aminopyridine in the presence of ruthenium catalysts.

2. Experimental

2.1. Preparation of benzimidazolium sulfonates

The zwitterionic carbene precursors **L1-L10** were obtained in a three step procedure according to Scheme 1. The *N*-alkyl or *N*-benzyl benzimidazole was first prepared by deprotonation of benzimidazole by NaH in THF at room temperature for 1 h. The resulting sodium benzimidazolate was reacted with the appropriate alkyl or benzyl halide in refluxing THF during 24 h. The resulting *N*-alkyl or *N*-benzyl-benzimidazole was isolated and purified as a white solid. 1-Substituted benzimidazole and 1,3-propanesultone were then dissolved in acetonitrile and refluxed during 72 h. The benzimidazole sulfonate salts **L1-L10** were isolated as solids in good to excellent yields.



Scheme 1. Synthesis of benzimidazolium sulfonate salts **L1-L10**

2.2. Catalytic reactions

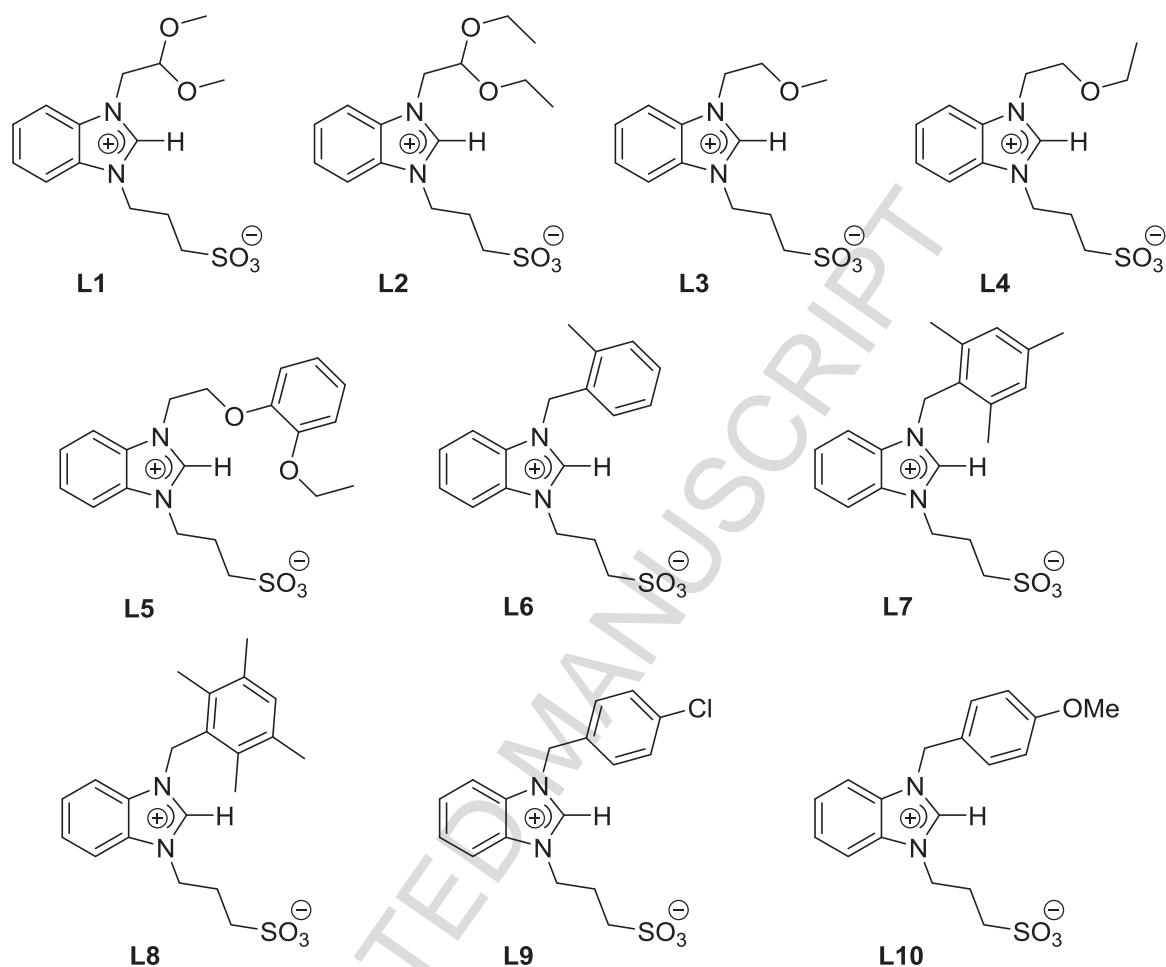
The alcohol derivative (1.6 mmol) was added to a stirred solution of aromatic amine (1 mmol) in a Schlenk tube. Subsequently, $t\text{BuOK}$ (1 mmol), the preligand (**L**) (1 mol%) and $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5 mol%) were added and the sealed Schlenk tube was stirred at 120 °C for 24 h. The crude mixture was collected by addition of CH_2Cl_2 (2 ml) for GC analysis, and

the product was then purified by column chromatography (petroleum ether/Et₂O or EtOAc) to afford the pure secondary amine.

3. Results and discussion

3.1. Preparation of benzimidazolium sulfonate salts

A library of 10 benzimidazolium sulfonate salts **L1-L10** has been prepared (Scheme 2). Each of them is equipped with a 1-*n*-propylsulfonate group linked to one nitrogen atom. The other nitrogen atom is substituted either by an aliphatic ether or an acetal functionality, or a benzylic group diversely substituted on the phenyl ring. The acetal groups are in principle stable in basic conditions and the oxygen atoms might be useful for hydrogen bonding or transfer. As far as the phenyl groups are concerned it has been previously shown that they can easily substitute a coordinated *p*-cymene ligand on a ruthenium(II) center upon thermal treatment [30].



L1-L10 are soluble in water and protic solvents; they were characterized by ^1H and ^{13}C NMR, and gave satisfactory elemental analysis. The benzimidazolium fragment showed characteristic C(2)-*H* proton chemical shift at 8.86-9.64 ppm associated to the ^{13}C NMR chemical shift of the C(2) carbon atom deshielded at 140-150 ppm (Table A.1). These chemical shifts are typical of all types of benzimidazolium salts including less functionalized ones. The ^1H NMR spectra of the linear *n*-propylsulfonate group is clearly identified by a triplet at 4.5-4.8 ppm for NCH_2 , another triplet at 2.8-3.0 ppm for CH_2SO_3 , and a pentuplet centered at 2.4 ppm for the internal CH_2 group, all coupling constants being close to 7 Hz.

3.2. Catalytic application in alkylation of aniline derivatives with alcohols

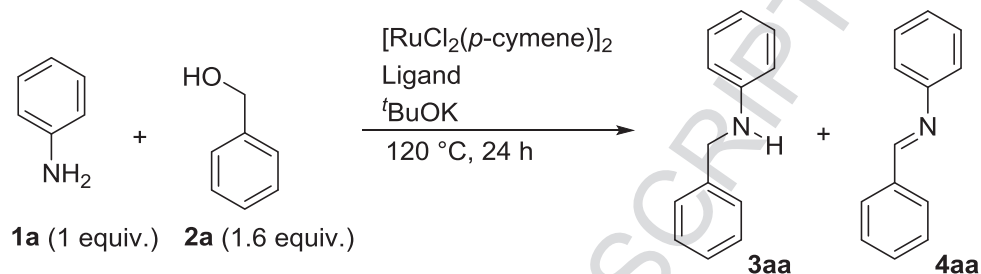
In order to evaluate the potential of carbene sulfonate ligands in hydrogen borrowing processes, we associated these ligands with $[\text{RuCl}_2(p\text{-cymene})]_2$, a very established precursor of efficient catalytic systems for this type of reaction [26], and studied their ability to achieve benzylation of aniline with benzyl alcohol as a model reaction. Aniline being a weak base ($\text{pK}_a = 4.6$), the benzimidazolium sulfonate salts **L1-L10** were deprotonated by $t\text{BuOK}$ in the presence of the ruthenium source to generate a catalytic system *in situ*.

The reaction were carried out at 120 °C for 24 h in neat conditions with 0.5 mol% of ruthenium dimer and 1 mol% of benzimidazolium sulfonate in the presence of a slight excess of benzyl alcohol. The results presented in Table A.1 show that all the ligand precursors led to high conversion with the amine **3a** as the major product, the imine **4a** being detected only as traces amount in some cases.

The influence of various parameters was then studied using the ligand precursor **L1** (Table 1). Up to 90% conversion were obtained with 15 mol% of $t\text{BuOK}$ (entries 1-4) and full conversion with high selectivity in favor of the amine could be obtained only when the ligand was added and a stoichiometric amount of $t\text{BuOK}$ was used (entries 6, 7, 13), which was in accordance with many previous results starting from aniline, and indicated that this strong base was not only useful for carbene generation but also accelerated imine hydrogenation (entries 5, 6). It is noteworthy that in the absence of base, a 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine pincer ruthenium complex led to the selective formation of imines from alcohols and aliphatic amines [31]. Decreasing the reaction temperature or the catalyst loading had a detrimental effect on both conversion and selectivity towards amine formation. It is also worth mentioning that the benzylation tolerated water as solvent (entry 12) and was also efficiently performed in toluene with high selectivity (entry 13). An excess of alcohol (1.6 equivalent) was required to achieve complete conversion of aniline. Indeed, potassium benzoate was formed as an undesired side product of this reaction resulting from Tishchenko or Cannizzaro disproportionation reaction from the intermediate benzaldehyde in the presence of $t\text{BuOK}$ and water arising from imine formation. It is noteworthy that in the presence of the benzimidazolium salt and base but in the absence of ruthenium precursor, no reaction took place (entry 15). Only 24% conversion was obtained in the presence of the metallic precursor and proligand showing the important role of $t\text{BuOK}$ in this catalytic system (entry 16). 72% conversion with an amine/imine ratio of 90/10 was observed when the

ruthenium dimer and the base were used in the absence of ligand (entry 14) confirming the preponderant role of the base and the ligand for efficient alkylation of aromatic amines [32].

Table 1. Benzylation of aniline **1a** with benzyl alcohol **2a**

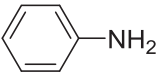
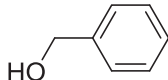
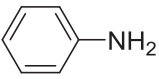
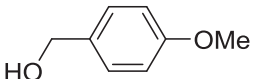
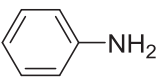
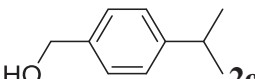
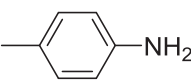
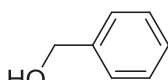
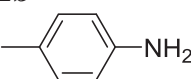
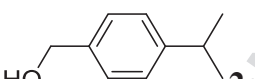
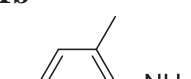
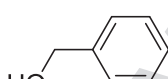


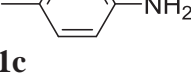

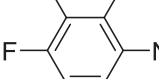
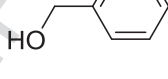
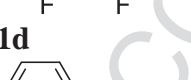
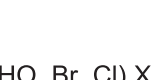
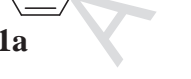
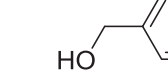


Entry	Ruthenium precursor (mol%)	Préligand (mol%)	$t\text{BuOK}$ (mol%)	Temp. ($^\circ\text{C}$)	Conv. (%)	3aa/4aa ratio
1	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L1 (1)	15	120	88 ^b	91/9
2	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.25)	L1 (0.5)	15	120	89	79/21
3	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L6 (1)	15	120	90 ^b	84/16
4	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L8 (1)	15	120	81 ^b	79/21
5	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L1 (1)	50	120	89	85/15
6	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L1 (1)	100	120	100	100/0
7	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L1 (1)	100	100	100	95/5
8	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L1 (1)	100	80	76	87/10
9	$[[\text{RuCl}_2(p\text{-cymene})]_2$ (0.25)	L1 (0.5)	100	120	97	95/5
10	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.0625)	L1 (0.125)	100	120	85	90/10
11	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.0625)	L1 (0.125)	100	120	98 ^c	92/8
12	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L1 (1)	100	120	68 ^d	98/2
13	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	L1 (1)	100	120	100 ^e	96/4
14	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	no	100	120	72	90/10
15	no	L1 (1)	100	120	0	-
16	$[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5)	no	0	120	24	96/4

^aAniline (1 mmol, 1 equiv.), benzyl alcohol (1.6 equiv.), $t\text{BuOK}$ as a base, no solvent, GC conversion based on the amine, **3/4** GC ratio, reaction time : 15 h, ^breaction time : 20 h, ^creaction time : 24 h, ^dwater as solvent (2 ml), ^etoluene as solvent (1 ml)

Based on this preliminary study, the scope of the reaction was investigated with substituted aromatic amines and benzylic alcohols applying our best experimental conditions (Table 2). Aniline reacted with *para*-substituted benzylic alcohols **2b** and **2c** to give the corresponding secondary benzylic anilines **3ab** and **3ac** in good yields and high selectivity (entries 2, 3). 4-Methylaniline (entries 4, 5) reacted similarly and provided excellent conversions and good isolated yields in **3ba** and **3bc** with benzyl alcohol **2a** and isopropylbenzyl alcohol **2c**.

Table 2. Scope of the benzylation of anilines with benzylic alcohols

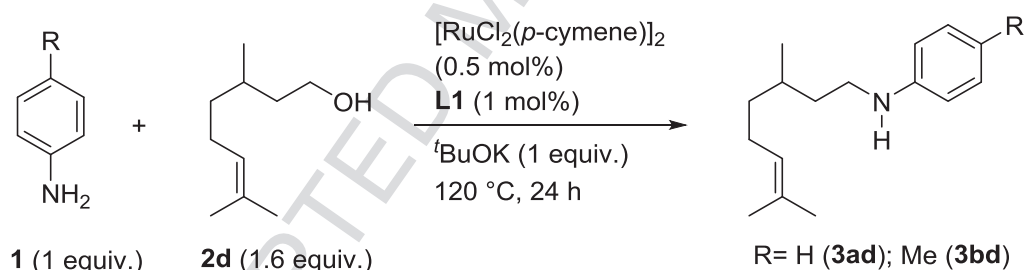
Entry	Amine 1	Alcohol 2	Conv.	3/4 ratio	3 Yield (%)
1	 1a	 2a	100	100/0	3aa (53%)
2	 1a	 2b	100	100/0	3ab (69%)
3	 1a	 2c	89	98/2	3ac (72%)
4	 1b	 2a	100	100/0	3ba (59%)
5	 1b	 2c	99	100/0	3bc (77%)
6	 1c	 2a	77	87/13	3ca (45%)
7	 1c	 2b	63	100/0	3cb (55%)
8	 1d	 2a	67	94/6	3da (54%)
9	 1a	(HO, Br, Cl) X 	0		
10	 1e	 R= H 2a , R= OMe 2b	0		
11	 1f	 R= H 2a , R= OMe 2b	0		

Aniline (1 mmol, 1 equiv.), benzyl alcohol (1.6 equiv.), ^tBuOK (1 mmol), [RuCl₂(*p*-cymene)]₂ (0.5 mol%), **L1** (1 mol%), no solvent, 120 °C, 24 h, GC conversion based on the amine, **3/4** GC ratio, isolated yield.

When 2,4-dimethylaniline **1c** was used as substrate, the reaction became more difficult and conversions of 77 and 63% only could be obtained with benzyl alcohol and 4-methoxybenzyl alcohol as respective partners after 24 h (entries 6, 7). 2,3,4,5,6-Pentafluoroaniline **1d** reacted also with benzyl alcohol **2a** to give the fluorinated aniline **3da** in 67% yield (entry 8). On the other hand, steric hindrance at the *ortho*-position of the aniline or the benzylic alcohol substrate

completely inhibited the reaction. More precisely, the *ortho*-disubstituted anilines **1e** and **1f** (entries 10, 11) and *ortho*-monosubstituted hydroxy or halogenated benzylic alcohols (entry 9) were unreactive.

With the objective of preparing aniline derivatives of natural products, we showed that under similar reaction conditions, citronellol **2d** reacted with aniline **1a** and 4-methylaniline **1b** to give the anilines **3ad** and **3bd** derived from terpene in 65 and 51% yield, respectively (Eq. 1).



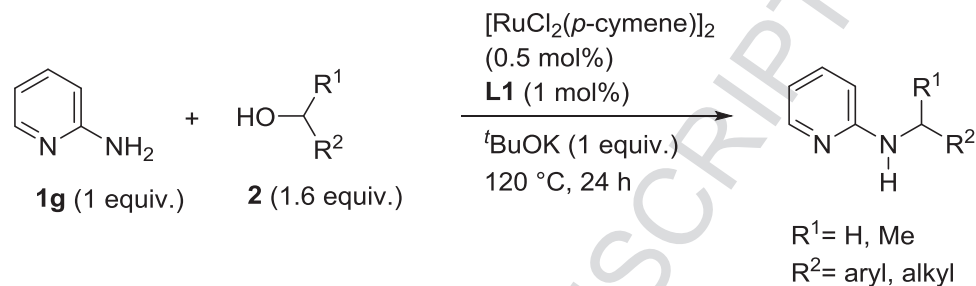
Equation 1. Terpenylation of anilines with citronellol

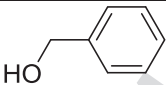
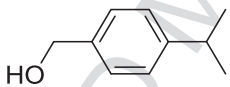
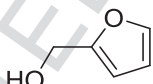
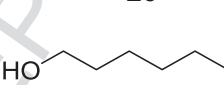

Alkylation of heteroaromatic amines such as aminoquinazolines, aminopyrimidines, aminoazoles or aminopyridine by alcohols have not been studied extensively in homogeneous catalysis and most of the successful results have been obtained with iridium catalysts [6, 33, 34]. With ruthenium catalysts, only a few examples of alkylation of 2-aminopyridine with alcohols have been recently reported with ruthenium complexes featuring tridentate (C,N,N) [24] ligand and cationic ruthenium(arene) complex equipped with a chelating pyridine-carbene ligand [27].

In the presence of our optimized catalytic system based on $[\text{RuCl}_2(p\text{-cymene})]_2$ and the carbene sulfonate ligand derived from **L1**, the primary heteroaromatic 2-aminopyridine reacted readily with various alcohols to selectively give the *N*-monoalkylated secondary amines (Table 3). Primary benzylic alcohols gave excellent yields of *N*-alkylated 2-aminopyridines and the products **3ga**, **3gc**, and **3ge** were isolated in 80, 75 and 60% yield, respectively. Alkylation with the purely aliphatic 1-hexanol was also possible in satisfactory

yield but with the secondary alcohols **2g** the conversion was lower and required 30 equiv. of isopropanol to reach 75% yield.

Table 3. *N*-Alkylation of 2-aminopyridine **1g**



Entry	Alcohol 2	Conv. (%)	3 Yield (%)
1	 2a	97	3ga (80%)
2	 2c	100	3gc (75%)
3	 2e	94	3ge (60%)
4	 2f	91	3gf (55%)
6	 2g	75 ^a	3gg (50%)

^a 30 equiv. of isopropanol

The ruthenium(carbene) complex $\text{RuCl}_2(p\text{-cymene})(N,N'\text{-bis(mesityl)imidazolyliidene})$ featuring aryl substituents directly connected to the nitrogen atoms of the carbene is known to catalyze the formation of amides from alcohols and primary aliphatic amines including aniline at a lower extend, in the presence of 15 mol% of $t\text{BuOK}$ [28]. Recently, ruthenium complexes such as $(N,N\text{-bis(benzyl)benzimidazolyliidene})$ - and $(N,N\text{-bis(isopropyl)benzimidazolyliidene})$ - $\text{RuCl}_2(p\text{-cymene})$ equipped with *N*-alkyl or/and *N*-benzyl NHC ligands with no chelating or hemilabile group on the NHC, have revealed good catalytic properties for the alkylation of anilines with various alcohols under neat conditions at 130 °C with 5 mol% catalyst loading without additional base [35]. The presence of the sulfonate group in our NHC precursors does

not seem to be essential in terms of reactivity, but contributes to promote the formation of amines rather than imines or amides. All these results show that the nature of the NHC carbene ligand is crucial for the ruthenium-catalyzed selective alkylation of anilines by alcohols with hydrogen borrowing processes.

However, at the moment, the most efficient catalytic systems for alkylation of aromatic amines operating under really mild conditions are based on iridium catalysts. They include reactions carried out in diglyme at 70 °C in the presence of ^tBuOK [16], a few examples at 50 °C in toluene/dichloromethane as solvent in the absence of an extra base [10], and even some scarce examples at room temperature in the presence of ^tBuOK under solvent-free conditions with 1 mol% catalyst loading [20].

Attempts to generate ruthenium complexes with a chelating carbene sulfonate ligand from [RuCl₂(*p*-cymene)]₂ as metal source and a silver carbene prepared from **L1** and Ag₂O have failed but further studies are currently under investigation.

In summary, we have prepared a library of new benzimidazolium sulfonate salts from *N*-substituted benzimidazoles and 1,3-propanesultone. The catalytic systems generated *in situ* from these salts and [RuCl₂(*p*-cymene)]₂ in the presence of ^tBuOK are efficient in hydrogen borrowing processes and make possible the selective monoalkylation of primary aromatic amines such as substituted anilines and 2-aminopyridine with a variety of alcohols under neat conditions at 120 °C with low catalyst loading. The scope and limitations mainly due to steric effects have been established.

Acknowledgement

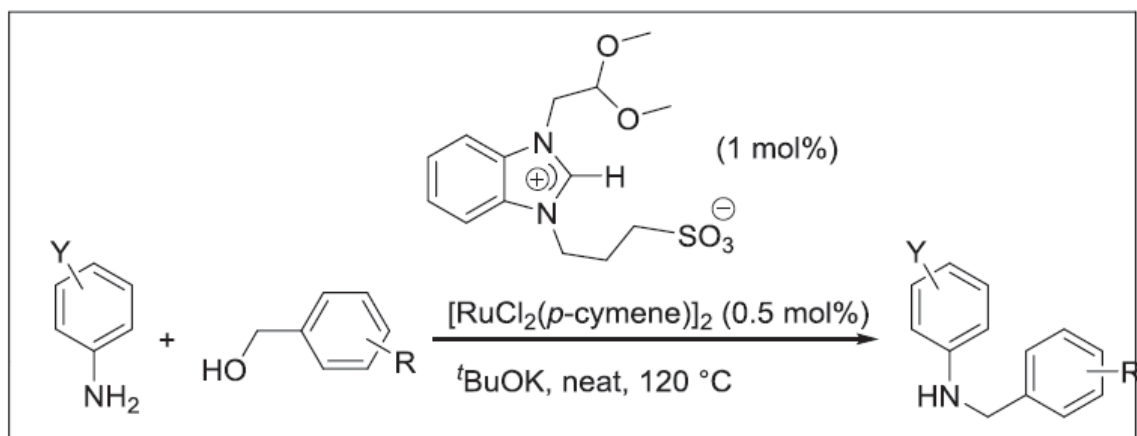
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References

- [1] Amines: Synthesis, Properties and Applications; S. A. Lawrence Ed.; Cambridge University Press, Cambridge, 2004.
- [2] Q. Yang, Q. Wang, Z. Yu, Chem. Soc. Rev. 44 (2015) 2305-2329.
- [3] R. Yamaguchi, K.-i Fujita, M. Zhu, Heterocycles 81 (2010) 1093-1140.
- [4] G. Guillena, D. J. Ramon, M. Yus, Chem. Rev. 110 (2010) 1611-1641.
- [5] G. E. Dobereiner, R. H. Crabtree, Chem. Rev. 110 (2010) 681-703.
- [6] T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, Dalton Trans. (2009) 753-762.
- [7] K.-i. Fujita, Y. Enoki, R. Yamaguchi, Tetrahedron 64 (2008) 1943-1954.
- [8] H. Aramoto, Y. Obara, Y. Ishii, J. Org. Chem. 74 (2009) 628-633.
- [9] R. Kawahara, K.-i. Fujita, R. Yamaguchi, Adv. Synth. Catal. 353 (2011) 1161-1168.
- [10] A. Bartoszewicz, R. Marcos, S. Sahoo, A. K. Inge, X. Zou, B. Martin-Matute, Chem. Eur. J. 18 (2012) 14510-14519.
- [11] J. Norinder, A. Börner, ChemCatChem 3 (2011) 1407-1409.
- [12] K.-T. Huh, Y. Tsuji, M. Kobayashi, F. Okuda, Y. Watanabe, Chem. Lett. (1988) 449-452.
- [13] S. G. Shim, C. H. Doh, B. W. Woo, H. S. Kim, K. T. Huh, W. H. Park, H. Lee, J. Mol. Catal. 62 (1990) L11-L15.
- [14] C. S. Cho, B. T. Kim, H. J. Choi, T. J. Kim, S. C. Shim, Tetrahedron 59 (2003) 7997-8002.
- [15] D. Wang, K. Zhao, C. Xu, H. Miao, Y. Ding, ACS Catal. 4 (2014) 3910-3918.
- [16] S. Ruch, T. Irrgang, R. Kempe, Chem. Eur. J. 20 (2014) 13279-13285.
- [17] K. D. Yuan, F. Jiang, Z. Sahli, M. Achard, T. Roisnel, C. Bruneau, Angew. Chem. Int. Ed. 51 (2012) 8876-8880.
- [18] D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito, R. H. Crabtree, Organometallics 28 (2009) 321-325.
- [19] A. Pontes da Costa, M. Viciano, M. Sanau, S. Merino, J. Tejada, E. Peris, B. Royo, Organometallics 27 (2008) 1305-1309.
- [20] J.-Q. Li, P. G. Andersson, Chem. Commun. 49 (2013) 6131-6133.
- [21] R. A. T. M. Abbenhuis, J. Boersma, G. van Koten, J. Org. Chem. 63 (1998) 4282-4290.
- [22] S. Agrawal, M. Lenormand, B. Martin-Matute, Org. Lett. 14 (2012) 1456-1459.
- [23] D. Weickmann, W. Frey, B. Plietker, Chem. Eur. J. 19 (2013) 2741-2748.

- [24] V. R. Jumde, L. Gonsalvi, A. Guerriero, M. Peruzzini, M. Taddei, *Eur. J. Org. Chem.* (2015) 1829-1833.
- [25] S. Naskar, M. Bhattacharjee, *Tetrahedron Lett.* 48 (2007) 3367-3370.
- [26] M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson, J. M. J. Williams, *J. Am. Chem. Soc.* 131 (2009) 1766-1774.
- [27] F. E. Fernandez, M. C. Puerta, P. Valerga, *Organometallics* 31 (2012) 6868-6879.
- [28] Y. Zhang, C. Chen, S. C. Ghosh, Y. Li, S. H. Hong, *Organometallics* 29 (2010) 1374-1378.
- [29] F. Jiang, M. Achard, C. Bruneau, *Adv. Organometal. Chem.* 62 (2014) 159-218.
- [30] B. Cetinkaya, S. Demir, I. Özdemir, L. Toupet, D. Sémeril, C. Bruneau, P. H. Dixneuf, *Chem. Eur. J.* **2003**, 9, 2323-2330.
- [31] B. Gnanaprakasam, J. Zhang, D. Milstein, *Angew. Chem. Int. Ed.* 49 (2010) 1468-1471.
- [32] A. B. Enyong, B. Moasser, *J. Org. Chem.* 79 (2014) 7553-7563.
- [33] F. Li, L. Chen, Q. Kang, J. Cai, G. Zhu, *New J. Chem.* 37 (2013) 624-631.
- [34] B. Blank, S. Michlik, R. Kempe, *Adv. Synth. Catal.* 351 (2009) 2903-2911.
- [35] S. P. Shan, X. Xiaoke, B. Gnanaprakasam, T. T. Dang, B. Ramalingam, H. V. Huynh, A. M. Seayad, *RSC Adv.* 5 (2015) 4434-4442.

Graphical Abstract



Highlights

- New benzimidazolium sulfonate salts
- *In situ* generated catalyst from $[\text{RuCl}_2(p\text{-cymene})]_2$ and benzimidazolium sulfonate
- *N*-alkylation of aromatic amines with alcohols *via* hydrogen borrowing process